# POLYMERIZATION PROCESS

This invention relates to improvements in
metallocene catalysed ethylene polymerisations which
take place in the presence of hydrogen.  In particular,
the invention relates to the surprising finding that
hydrogen can deactivate the catalyst employed in the
polymerisation reaction unless contact between hydrogen
and the catalyst is eliminated prior to their entry into
the reactor where the polymerisation takes place.

In most Ziegler-Natta and metallocene
polymerisations, hydrogen is used to regulate the
molecular weight of the formed polymer as is well known
in the art. In case of metallocenes, hydrogen
sensitivity is 100-1000 times higher than that observed
for Zielger-Natta catalysts.

For slurry polymerisation, there are two common
ways employed to feed the catalyst, hydrogen, monomers,
diluent etc into the slurry polymerisation reactor.  In
one case, hydrogen, ethylene, comonomer and diluent
streams are combined and passed into the reactor.  The
catalyst stream is combined with a small amount of
diluent and passed separately into the reactor.

In a second, less common set up, the hydrogen,
ethylene and comonomer stream is combined with the
catalyst/diluent stream just prior to reactor entry and
a single feed stream enters the reactor.

The polymer slurry recovered at the outlet of the
slurry polymerisation reactor is typically directed into
polymer recovery or a further polymerisation stage, e.g.
a gas phase polymerisation, and the hydrocarbons, such
as the diluent, monomer(s) and comonomers, and hydrogen
are separated from the polymer slurry. The recovered
hydrocarbons may then be directed to a series of
purification and separation stages, where the different
components may be separated from one another.

Eventually, most of the recovered hydrocarbons are recycled back into the polymerisation reactor.

Hence, the main part of the diluent introduced into a polymerisation reactor is typically recycled and only up to 5% of the diluent is absolutely pure, i.e. is not recycled. The recycled diluent may contain small amounts of residual monomer(s), comonomers and hydrogen as impurities.

When particularly active catalysts are introduced into a polymerisation reactor, it is conventional that contact between the monomer(s) and the catalyst before entry into the polymerisation reactor is avoided or minimised. This is to eliminate the risk of polymerisation in the feed lines, eventually leading to plugging of the feed line and reactor shutdown. For this reason and as discussed above, the feed is often divided so that part of the diluent and monomer(s) are introduced along one pipe line into the reactor while the remaining components are introduced along another line, e.g. the line from a prepolymerisation reactor. This means that the catalyst is often added into the reactor potentially in recycled diluent.

The catalyst is usually added into a slurry polymerisation process as a slurry. For example, the catalyst is suspended in diluent and transferred into a catalyst feed vessel. This vessel may be agitated to maintain homogeneous the slurry of the catalyst in diluent, but it may also be non-agitated so that the catalyst is allowed to settle and form a deposit at the bottom of the vessel. The slurry or deposit is then metered into the polymerisation reactor by using conventional methods, like shot injectors as disclosed in EP 428054 and EP 428056. In such arrangements the catalyst may remain in contact with the diluent for a long time, e.g. from several hours up to 1 to 2 days.

It has been surprisingly found that when there is contact between a metallocene catalyst and hydrogen

prior to catalyst entry into the reactor where
polymerisation takes place, a serious deactivation of
metallocene catalyst occurs. The seriousness of the
deactivation varies from catalyst to catalyst but in all
metallocenes tested significant deactivation occurs. It
is believed that this is the first time that this effect
has been noted and hence the inventors have identified a
problem not previous known.

The inventors have found therefore that it is
essential to eliminate any contact between the catalyst
and hydrogen prior to the components entering the
polymerisation reactor. This has significant
ramifications for polymerisation reactor set up, in
particular on industrial scale where recycling of
components is routine for environmental and economic
reasons.

In the first of the two common feed methods
described above, whilst the main hydrogen feed does not
precontact the catalyst, since the diluent stream is
normally recycled this is likely to contain traces of
hydrogen and hence the catalyst is exposed to hydrogen
prior to reactor entry. In the second scenario, the
catalyst is also exposed to recycled diluent leading to
potential for catalyst deactivation.

It is believed that this is the first time this
effect has been noted although some polymer chemists
appear to have inadvertently added catalyst and hydrogen
to a reactor in separate feeds without appreciating the
ramifications of the steps they were taking. Hence, in
EP-A-781300 polymerisation is effected in a fluidised
bed reactor with a gaseous feed stream comprising
ethylene and hydrogen. The catalyst is injected into
the bed directly. This polymerisation is not a slurry
phase polymerisation and there is no mention of the
prevention of catalyst deactivation. Moreover, a
diluent is not employed. Other chemists may have used
direct catalyst injection to a reactor in bench scale or

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pilot plant where recycling of diluent is not normal but
on industrial scale where recycling is important this
deactivation effect is critical.

    Hence, viewed from one aspect the invention
5   provides a process for the polymerisation of ethylene
and optionally at least one $C_{3-20}$ alpha olefin comonomer
in the slurry phase or solution phase in a
polymerisation reactor having a polymer outlet stream, a
procatalyst or catalyst feed stream and a hydrogen feed
10  stream, said polymerisation being effected in the
presence of a metallocene catalyst, a diluent and
hydrogen, characterised in that said diluent is recycled
from said outlet stream to said hydrogen feed stream,
said catalyst feed stream is free of hydrogen, said
15  hydrogen feed stream is free of catalyst and said
catalyst feed stream is free of recycled diluent.

    Alternatively viewed the invention relates to a
process for the polymerisation of ethylene and
optionally at least one $C_{3-20}$ alpha olefin comonomer in
20  the slurry phase or solution phase in a polymerisation
reactor comprising the steps of:

    continuously introducing ethylene and optionally at
least one $C_{3-20}$ alpha olefin comonomer into said reactor;

    continuously introducing diluent into said reactor;
25      continuously introducing hydrogen into said
reactor;

    continuously or intermittently introducing a
mixture of diluent and metallocene catalyst into said
reactor;
30      operating the reactor to form a polymer slurry or
solution;

    continuously or intermittently removing said
polymer slurry or solution from said reactor;

    subjecting the withdrawn slurry or solution to
35  separation treatment where at least part of the diluent
therein is separated from the polymer;

recycling at least part of said separated diluent
into the diluent feed;

wherein the diluent feed is free of catalyst and
said mixture of diluent and metallocene catalyst is free

5   of recycled diluent.

Viewed from another aspect the invention provides a
method for preventing metallocene catalyst deactivation
in an ethylene polymerisation process effected in the
presence of hydrogen, the improvement comprising feeding

10  said metallocene catalyst to a polymerisation reactor in
a feed stream in which hydrogen is absent.

Viewed from a further aspect the invention
comprises use of at least two feed streams, a first
stream comprising a metallocene catalyst and being free

15  of hydrogen and a second stream comprising hydrogen and
being free of metallocene catalyst to prevent
metallocene catalyst deactivation in ethylene
polymerisation.

The process of the invention should preferably be

20  carried out on an industrial scale.

The term "metallocene catalyst" is used herein to
denote the reaction product of a metallocene procatalyst
and a cocatalyst.  It is possible for the metallocene
procatalyst and the cocatalyst to be reacted to form the

25  actual catalytic species (i.e. the metallocene catalyst)
prior to injection into the reactor or this reaction can
be effected in the reactor itself.  In this latter
scenario, the metallocene procatalyst feed to the
reactor should be free of hydrogen/recycled diluent and

30  the cocatalyst should be fed to the reactor separately
under known conditions.

Hydrogen may be fed into the reactor with recycled
diluent alone or may be fed to the reactor along with
monomer and/or comonomer or combinations thereof.  Most

35  commonly, hydrogen is continuously fed to the reactor
with recycled diluent, monomer (ethylene) and comonomer,
i.e. the hydrogen feed stream preferably comprises

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hydrogen, ethylene, optional comonomer and recycled
diluent. Hydrogen must not however, be fed to the
reactor with the metallocene catalyst. In order to
avoid catalyst deactivation it is essential to avoid
5     contact between hydrogen and metallocene catalyst unless
the monomer is additionally present. Hence, recycled
diluent containing traces of hydrogen should not be used
to slurry the metallocene catalyst prior to its
injection into the polymerisation reactor.
10        The catalyst is fed to the reactor in a separate
feed stream, e.g. via a catalyst feed vessel and may be
conveyed to the reactor in a diluent either continuously
or intermittently. However, the diluent employed in the
catalyst feed must not be recycled to ensure that the
15    diluent is hydrogen free. Conventionally, diluent is
recycled from the outlet stream for economic reasons and
employed again in both catalyst and hydrogen feed
streams. The present inventors have found that even
after purification, the recycled diluent contains traces
20    of hydrogen which can detrimentally affect catalyst
performance causing deactivation. This is especially
true in the catalyst feed vessel, where the catalyst may
remain in contact with recycled diluent for a prolonged
period, e.g. 2 hours to 1 to 2 days.
25        By deactivation is meant that the catalyst suffers
a loss of activity, i.e. the amount of polymer produced
in a given time is less when precontact of hydrogen and
the catalyst occurs. Precontact has also been found to
cause the catalyst to have an increased induction time.
30    When no contact between catalyst and hydrogen takes
place the catalyst typically starts catalysing the
polymerisation reaction the instant the reaction is
initiated. However, when precontact occurs the
inventors have surprisingly found that induction times
35    of at least 5 minutes, e.g. at least 10 minutes are
observed, i.e. time when the catalyst does not catalyse
the polymerisation reaction.

Diluent recycling and purification can be achieved using known techniques. For example, first the diluent may be separated from the polymer. This may be done by any means known in the art, such as centrifugation and

5   evaporation. The diluent may be selected from inert hydrocarbon compounds, which readily can be separated from the monomers and other components used in polymerisation, like hydrogen. Preferably, the diluent is an alkane containing from 2 to 20 carbon atoms. More

10  preferably, the diluent is a low-boiling alkane containing from 3 to 6 carbon atoms, like propane, n-butane, isobutane, n-pentane, or n-hexane. Especially preferred are propane, n-butane and isobutane.

After the diluent is separated from the polymer, it

15  may be subjected to different process steps to separate the residual monomer(s), hydrogen, catalyst components, impurities like moisture, and other compounds that may be present. These process steps include, among others, distillation, extraction and treatment in catalytic

20  beds. It is worth noting, however, that each such process step increases both the investment cost and the operating cost of the polymerisation plant.

The recovered diluent is then pressurised, e.g. by using a pump or a compressor, and passed into the

25  hydrogen stream.

The amount of hydrogen in the recycled diluent depends on the product that is made and the nature of the catalyst employed. When a metallocene catalyst is used, the hydrogen content in the diluent may range from

30  0.1 to 500 ppm (parts per million, based on the number of moles of each component in the diluent), preferably 0.2 to 200 ppm, more preferably 0.5 to 50 ppm, or 1 to 20 ppm (depending on the melt index (MFR) of the polymer that is produced) unless special hydrogen separation

35  techniques are employed. When a Ziegler catalyst is used, the hydrogen concentration in the diluent may be up to 3% by mole, provided that no special hydrogen

separation is done.  Therefore, during transitioning
between a Ziegler-Natta catalyst to a metallocene
catalyst the risk of deactivation is incceased, if
recycled diluent is used in the catalyst handling.

5       In a further preferred embodiment therefore, the
process of the invention is employed where transitioning
between Ziegler-Natta and metallocene catalysts takes
place.  Since hydrogen concentration in the reactor is
greater during Ziegler-Natta catalysis, the amount of

10  residual hydrogen in the recycled diluent is higher.
When the transitioning begins, the metallocene catalyst
would conventionally be slurried with recycled diluent
(i.e. containing a high level of hydrogen) before being
added to the reactor.  Such slurrying can cause

15  deactivation.  It is especially important therefore to
avoid diluent recycling into the catalyst feed stream
where transitioning between Ziegler-Natta and
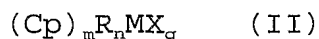metallocene catalysts takes place.

        The polymerisation reaction of the invention takes

20  place in the solution phase or preferably the slurry
phase, preferably in a loop reactor as is well known in
the art and under conditions described fully below.  The
concentration of hydrogen used in polymerisation is
selected based on the melt index of the polymer that is

25  produced.  Typically, the molar ratio of hydrogen to
ethylene is from 1 to 2000 moles of hydrogen per million
moles of ethylene, preferably from 5 to 1000, more
preferably from 10 to 500 and in particular 20 to 200
moles of hydrogen per million moles of ethylene.  The

30  amount of monomer, comonomer, diluent and catalyst
employed may vary and will be readily determined by the
skilled chemist.

        In a highly preferred embodiment the catalyst is
prepolymerised as is well known in the art.

35      The slurry phase polymerisation of the invention
should preferably be followed by a gas phase
polymerisation.  Such technology involving slurry phase/

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gas phase polymerisation stages has been developed by
Borealis and is called Borstar Technology. The slurry
phase may however be the only stage in the
polymerisation or may be followed by further slurry
5   stages.

The metallocene procatalyst may have a formula II:

$$(Cp)_m R_n MX_q \qquad (II)$$

10  wherein:

each Cp independently is an unsubstituted or
substituted and/or fused homo- or heterocyclopentadienyl
ligand, e.g. substituted or unsubstituted
cyclopentadienyl, substituted or unsubstituted indenyl
15  or substituted or unsubstituted fluorenyl ligand; the
optional one or more substituent(s) being independently
selected preferably from halogen, hydrocarbyl (e.g. C1-
C20-alkyl, C2-C20-alkenyl, C2-C20-alkynyl, C3-C12-
cycloalkyl, C6-C20-aryl or C7-C20-arylalkyl), C3-C12-
20  cycloalkyl which contains 1, 2, 3 or 4 heteroatom(s) in
the ring moiety, C6-C20-heteroaryl, C1-C20-haloalkyl, -
SiR"$_3$, -OSiR"$_3$, -SR", -PR"$_2$ or -NR"$_2$, each R'' is
independently a hydrogen or hydrocarbyl, e.g. C1-C20-
alkyl, C2-C20-alkenyl, C2-C20-alkynyl, C3-C12-cycloalkyl
25  or C6-C20-aryl; or e.g. in case of -NR"$_2$, the two
substituents R" can form a ring, e.g. five- or six-
membered ring, together with the nitrogen atom wherein
they are attached to;

R is a bridge of 1-7 atoms, e.g. a bridge of 1-4 C-
30  atoms and 0-4 heteroatoms, wherein the heteroatom(s) can
be e.g. Si, Ge and/or O atom(s), whereby each of the
bridge atoms may bear independently substituents, such
as C1-C20-alkyl, tri(C1-C20-alkyl)silyl, tri(C1-C20-
alkyl)siloxy or C6-C20-aryl substituents); or a bridge
35  of 1-3, e.g. one or two, hetero atoms, such as silicon,
germanium and/or oxygen atom(s), e.g. -SiR$^1_2$-, wherein

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each $R^1$ is independently C1-C20-alkyl, C6-C20-aryl or
tri(C1-C20-alkyl)silyl- residue, such as trimethylsilyl;

M is a transition metal of Group 3 to 10,
preferably of Group 4 to 6, such as Group 4, e.g. Ti, Zr
5     or Hf, especially Hf

each X is independently a sigma-ligand, such as H,
halogen, C1-C20-alkyl, C1-C20-alkoxy, C2-C20-alkenyl,
C2-C20-alkynyl, C3-C12-cycloalkyl, C6-C20-aryl, C6-C20-
aryloxy, C7-C20-arylalkyl, C7-C20-arylalkenyl, -SR", -
10    $PR"_3$, $-SiR"_3$, $-OSiR"_3$, $-NR"_2$ or  $-CH_2-Y$, wherein Y is C6-
C20-aryl, C6-C20-heteroaryl, C1-C20-alkoxy, C6-C20-
aryloxy, $NR"_2$, -SR", $-PR"_3$, $-SiR"_3$, or $-OSiR"_3$;

each of the above mentioned ring moiety alone or as
a part of another moiety as the substituent for Cp, X,
15    R" or $R^1$ can further be substituted e.g. with C1-C20-
alkyl which may contain Si and/or O atoms;

n is 0, 1 or 2, e.g. 0 or 1,
m is 1, 2 or 3, e.g. 1 or 2,
q is 1, 2 or 3, e.g. 2 or 3,
20    wherein m+q is equal to the valency of M.

Suitably, in each X as $-CH_2-Y$, each Y is
independently selected from C6-C20-aryl, $NR"_2$, $-SiR"_3$ or
$-OSiR"_3$. Most preferably, X as $-CH_2-Y$ is benzyl. Each X
other than $-CH_2-Y$ is independently halogen, C1-C20-alkyl,
25    C1-C20-alkoxy, C6-C20-aryl, C7-C20-arylalkenyl or $-NR"_2$
as defined above, e.g. $-N(C1-C20-alkyl)_2$.

Preferably, q is 2, each X is halogen or $-CH_2-Y$, and
each Y is independently as defined above.

Cp is preferably cyclopentadienyl, indenyl,
30    tetrahydroindenyl or fluorenyl, optionally substituted
as defined above and may further bear a fused ring of 3
to 7 atoms, e.g. 4, 5 or 6, which ring may be aromatic
or partially saturated.

In a suitable subgroup of the compounds of formula
35    II, each Cp independently bears 1, 2, 3 or 4
substituents as defined above, preferably 1, 2 or 3,
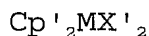such as 1 or 2 substituents, which are preferably

selected from C1-C20-alkyl, C6-C20-aryl, C7-C20-
arylalkyl (wherein the aryl ring alone or as a part of a
further moiety may further be substituted as indicated
above), -OSiR"$_3$, wherein R" is as indicated above,
5    preferably C1-C20-alkyl.

R, if present, is preferably a methylene, ethylene
or a silyl bridge, whereby the silyl can be substituted
as defined above, e.g. a (dimethyl)Si=,
(methylphenyl)Si= or (trimethylsilylmethyl)Si=; n is 0
10   or 1; m is 2 and q is two. Preferably, R" is other than
hydrogen.

A specific subgroup includes the well known
metallocenes of Zr, Hf and Ti with two eta$^5$-ligands which
may be bridged or unbridged cyclopentadienyl ligands
15   optionally substituted with e.g. siloxy, or alkyl (e.g.
C1-6-alkyl) as defined above, or with two unbridged or
bridged indenyl ligands optionally substituted in any of
the ring moieties with e.g. siloxy or alkyl as defined
above, e.g. at 2-, 3-, 4- and/or 7-positions, preferred
20   bridges being ethylene or -SiMe$_2$.

Further preferred metallocenes include those of
formula


Cp'$_2$MX'$_2$
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wherein M is as hereinbefore defined; each X' is
halogen, diC$_{1-6}$-alkylamido, C$_{1-6}$ alkyl, benzyl or hydrogen;
each Cp' is a cyclopentadienyl or indenyl group
optionally substituted by one or more groups selected
30   from C$_{1-10}$ hydrocarbyl or siloxy (e.g. triC$_{1-6}$alkylsiloxy),
said Cp' groups being optionally bridged, e.g. via an
ethylene or dimethylsilyl link. Bis (n-
butylcyclopentadienyl) hafnium dichloride, bis (n-
butylcyclopentadienyl) zirconium dichloride and ethylene
35   bis (2-t-butyldimethylsiloxyindenyl) hafnium complexes
are particularly preferred.

The preparation of the metallocenes of the invention can be carried out according or analogously to the methods known from the literature and is within skills of a person skilled in the field. Thus for the preparation see e.g. EP-A-129 368, examples of compounds wherein the metal atom bears a -NR"$_2$ ligand see i.a. in WO-A-9856831 and WO-A-0034341. For the preparation see also e.g. in EP-A-260 130, WO-A-9728170, WO-A-9846616, WO-A-9849208, WO-A-9912981, WO-A-9919335, WO-A-9856831, WO-A-00/34341, EP-A-423 101 and EP-A-537 130.

Alternatively, in a further subgroup of the metallocene compounds, the metal bears a Cp group as defined above and additionally a eta$^1$ or eta$^2$ ligand, wherein said ligands may or may not be bridged to each other. Such compounds are described e.g. in WO-A-9613529, the contents of which are incorporated herein by reference.

Highly preferred metallocene procatalysts are those listed in the examples.

Metallocene procatalysts are generally used as part of a catalyst system which also includes a cocatalyst or catalyst activator, for example, an aluminoxane (e.g. methylaluminoxane (MAO), hexaisobutylaluminoxane and tetraisobutylaluminoxane) or a boron compound (e.g. a fluoroboron compound such as triphenylpentafluoroboron or triphentylcarbenium tetraphenylpentafluoroborate ($(C_6H_5)_3B^+B-(C_6F_5)_4$)).

Traditionally, the most widely used alumoxane is methylalumoxane (MAO), an alumoxane compound in which the R groups are methyls. MAO however is poorly characterised and relatively expensive and efforts have been made to use alumoxanes other than MAO. Thus, for example WO98/32775 (Borealis) proposes the use of metallocene procatalysts with alumoxanes in which R is a $C_{2-10}$ alkyl group, eg hexaisobutylalumoxane (HIBAO).

If desired the procatalyst, procatalyst/cocatalyst mixture or a procatalyst/cocatalyst reaction product may

be used in unsupported form or it may be precipitated
and used as such. However the metallocene procatalyst
or its reaction product with the cocatalyst is
preferably introduced into the polymerization reactor in
5  supported form, eg impregnated into a porous particulate
support as is well known in the art.

The support is preferably a metal or pseudo metal
oxide such as silica, alumina or zirconia or a mixed
oxide such as silica-alumina, in particular silica,
10  alumina or silica-alumina.

Especially preferably the support is a porous
material so that the metallocene may be loaded into the
pores of the support, e.g. using a process analogous to
those described in WO94/14856 (Mobil), WO95/12622
15  (Borealis) and WO96/00243 (Exxon). The particle size is
not critical but is preferably in the range 5 to 200 um,
more preferably 20 to 80 um.

Before loading, the particulate support material is
preferably calcined. The support may also be treated
20  with an alkylating agent before being loaded with the
metallocene as is known in the art. The support may
also carry the cocatalyst/ionic activator as is known in
the art.

The olefin polymerized in the method of the
25  invention is ethylene or ethylene and at least one
alpha-olefin, for example $C_{3-20}$ alpha-olefins, e.g,
propene, n-but-1-ene, n-hex-1-ene, 4-methyl-pent-1-ene,
n-oct-1-ene etc. The olefins polymerized in the method
of the invention may include any compound which includes
30  unsaturated polymerizable groups. Thus for example
unsaturated compounds, such as $C_{6-20}$ olefins (including
cyclic and polycyclic olefins (e.g. norbornene)), and
polyenes, especially $C_{6-20}$ dienes, may be included in a
comonomer mixture with lower olefins, e.g. $C_{2-5}$-olefins.
35  Diolefins (ie. dienes) are suitably used for introducing
long chain branching into the resultant polymer.
Examples of such dienes include, linear dienes such as

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1,5-hexadiene, 1,6-heptadiene, 1,8-nonadiene, 1,9-
decadiene, etc.

Comonomers, such as $C_{4-6}$ alkenes, will generally be
incorporated to contribute to the mechanical strength of

5    the polymer product.

Usually metallocene catalysts yield relatively
narrow molecular weight distribution polymers; however,
if desired, the nature of the monomer/monomer mixture
and the polymerization conditions may be changed during

10   the polymerization process so as to produce a broad
bimodal or multimodal molecular weight distribution
(MWD) in the final polymer product.  In such a broad MWD
product, the higher molecular weight component
contributes to the strength of the end product while the

15   lower molecular weight component contributes to the
processability of the product, e.g. enabling the product
to be used in extrusion and blow moulding processes, for
example for the preparation of tubes, pipes, containers,
films etc.

20       A multimodal MWD can be produced using a catalyst
material with two or more different types of active
polymerization sites, e.g. with one such site provided
by the metallocene on the support and further sites
being provided by further catalysts, e.g. Ziegler

25   catalysts, other metallocenes, etc. included in the
catalyst material.

For solution phase reactors, the reaction
temperature used will generally be in the range 130 to
270°C, the reactor pressure will generally be in the

30   range 20 to 400 bar and the residence time will
generally be in the range 0.1 to 1 hour.  The solvent
used will commonly be a hydrocarbon with a boiling point
in the range 80-200°C.

For slurry reactors, the reaction temperature will

35   generally be in the range 60 to 110°C (e.g. 85-110°C),
the reactor pressure will generally be in the range 5 to
80 bar (e.g. 50-65 bar), and the residence time will

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generally be in the range 0.3 to 5 hours (e.g. 0.5 to 2
hours). The diluent used will generally be an aliphatic
hydrocarbon having a boiling point in the range -70 to
+100°C. In such reactors, polymerization may if desired
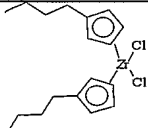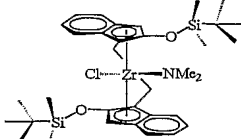5   be effected under supercritical conditions.

For gas phase reactors, the reaction temperature
used will generally be in the range 60 to 115°C (e.g. 70
to 110°C), the reactor pressure will generally be in the
range 10 to 25 bar, and the residence time will
10  generally be 1 to 8 hours. The gas used will commonly
be a non-reactive gas such as nitrogen together with
monomer (e.g. ethylene).

The invention will be described further with
reference to Figure 1. Polymerisation loop reactor (1)
15  has a polymer slurry outlet (3), catalyst feed inlet (5)
and hydrogen feed inlet (7). Diluent is recycled from
outlet (3) via recycling apparatus (9) in conduit (13)
to the inlet (7). The catalyst feed may derive from
prepolymerisation reactor (11).

20      Viewed from another aspect therefore, the invention
provides a slurry polymerisation reactor having a
polymer slurry outlet, catalyst feed inlet and hydrogen
feed inlet, said slurry outlet having a conduit
connecting to said hydrogen feed inlet adapted to allow
25  recycling of diluent from said polymer slurry to said
hydrogen feed.

All publications referred to herein are hereby
incorporated by reference.

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## Experimental procedures: Catalyst components:

*Table 1* Used Catalyst Components.

| | Structure | Background |
|---|---|---|
| Compound 1 | | $C_{18}H_{26}Cl_2Zr$<br>$M_w$ = 404,53 g mol$^{-1}$<br>Producer/trade name: Witco, EURECEN 5031 |
| Compound 2 | | $C_{34}H_{50}NO_2ClZrSi_2$<br>$M_w$ = 687,62 g mol$^{-1}$<br>Preparation EP 1137677 |
| Compound 3 | | $C_{18}H_{26}Cl_2Hf$<br>$M_w$ = 491.80 g mol$^{-1}$<br>C 43.96% H 5.33% Cl 14.42% Hf 36.29%<br>Producer/trade name: Witco, TA02823 |
| Activator | MAO | Albemarle 30w% MAO in toluene |
| Silica support 1 | Silica ($SiO_2$)<br>SP9-391 | Grace silica carrier, P.V. = 1.5 mL<br>(740 µmol OH /g $SiO_2$), BET S.A. 230-355 m$^2$/g. |
| Silica support 2 | Silica ($SiO_2$)<br>SP9-393A | Grace silica carrier, P.V. = 1.5 mL<br>(620 µmol OH /g $SiO_2$), BET S.A. 304-313 m$^2$/g. |

### *Hydrogen pre-contact test procedure*

Hydrogen pre-contact tests were carried out in 5.2 litre reactor. In these pre-contact tests hydrogen was added to the reactor batchwise and no extra hydrogen was added during the polymerisation. Hydrogen and catalyst were kept in the reactor ca. 20 minutes while reactor was heated and then the polymerisation was started normally.

**Table 2.** Hydrogen pre-contact polymerisation test procedure

| Step | |
|---|---|
| 1 | Add 1750 ml of isobutane to the reactor |
| 2 | Add catalyst from the feed vessel by flushing it through with 1750 ml isobutane |
| 3 | Add the amount of hydrogen needed from a pressure container. |
| 4 | Heat to +80 ºC, stirring 200 rpm |
| 5 | Set 1-hexene amount and purge pre mixing chamber with the<br>Desired ethylene/comonomer/ composition |
| 6 | Set stirring speed to 400 rpm |
| 7 | Adjust targeted pressure in reactor with the ethylene |
| 8 | After 60 min polymerisation, reaction was stopped by closing ethylene feed and flashing of the Isobutane diluent. |

Example 1

The catalyst was prepared by preparing complex solution of 103g compound 1 (see table 1) and 10.07 kg 30wt% MAO. Precontact time for metallocene/MAO was 2h at 25-27°C. 10 kg of this complex solution was impregnated slowly on

5      8000g of support 1 (see table 1). After 4h reaction at 25°C catalyst was dried by nitrogen purge at 55°C. After 6h drying ready catalyst was recovered. Ready made catalyst has Al/Zr =200 mol/mol.

10     Polymerisation was performed according to polymerisation procedure presented in table 2 with no precontact with $H_2$ and catalyst by using 251 mg of prepared catalyst. The yield of polymer was 731 g.

15     **Example 2**

Catalyst prepared according to Example 1 was used.

Polymerisation was performed according to polymerisation procedure presented in table 2 by using 275 mg of

20     prepared catalyst. The amount of hydrogen used during pre-contact time (20 min) was 30 bar/75 ml. The yield on polymer was 514 g.

**Example 3**

25     Catalyst was prepared by preparing complex solution of 305,9 mg compound 2 (see table 1) and 19,8 ml 30w% MAO and 4,4 ml toluene. Precontact time for metallocene/MAO was 60 min. 15 ml of this complex solution was impregnated slowly on 10 g of support 1 (see table 1).

30     After 1 h reaction at 24°C reaction temperature was raised to 70°C for 1h. Catalyst was dried by nitrogen purge at 70°C . After 3h  drying ready catalyst was recovered. Ready made catalyst has Al/Zr =200 mol/mol

35     Polymerisation was performed according to polymerisation procedure presented in table 2 but NO precontact of $H_2$

and catalyst by using 248 mg of prepared catalyst. The
yield on polymer was 740g.

**Example 4**

5   Catalyst prepared according to Example 3 was used.

Polymerisation was performed according to polymerisation
procedure presented in table 2 by using 233 mg of
prepared catalyst. The amount of hydrogen used during
10  precontact time (20 min) was 25 bar/75 ml. The yield on
polymer was 256 g.

**Example 5**

Catalyst was prepared by preparing complex solution of
15  156 g compound 3 (see table 1) and 12,6 kg 30w% MAO.
Precontact time for metallocene/MAO was 4 h / 25 °C.
12,6 kg kg of this complex solution was impregnated
slowly on 10 kg of support 2 (see table 1). After 4h
reaction at 25oC and additional 1 h reaction at 70 °C,
20  catalyst was dried by nitrogen purge at 70 °C . After 3h
drying ready catalyst was recovered. Ready made catalyst
has Al/Hf =200 mol/mol

Polymerisation was performed according to polymerisation
25  procedure presented in table 2 but NO precontact of H2
and catalyst by using 440 mg of prepared catalyst. The
yield on polymer was 382 g.

**Example 6**

30  Catalyst prepared according to Example 5 was used.
Polymerisation was performed according to polymerisation
procedure presented in table 2 by using 560 mg of
prepared catalyst. The amount of hydrogen used during
pre-contact time (20 min) was 25 bar/75 ml. The yield on
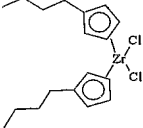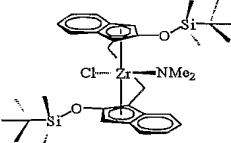35  polymer was 0 g.

**Example 7**

Catalyst prepared according to Example 5 was used.

Polymerisation was performed according to polymerisation procedure presented in table 2 by using 504 mg of prepared catalyst. The amount of hydrogen used during pre-contact time (20 min) was 30 bar/75 ml. The yield on polymer was 0 g.

*Summary of the examples*

***Table 3.*** Polymerisation results from hydrogen pre-contact tests.

| | Example 1 | Example 2 | Example 3 | Example 4 | Example 5 | Example6 | Example7 |
|---|---|---|---|---|---|---|---|
| Catalyst | Catalyst 1 | | Catalyst 2 | | Catalyst 3 | | |
| |  | |  | |  | | |
| Cat amount mg | 251 | 275 | 248 | 233 | 440 | 560 | 504 |
| $H_2$ | Continuos 2.8 mol/kmol | Precontact 30 bar/75 ml | Continuos 2.5 mol/kmol | Precontact 25 bar/75 ml | Continuos 3.2 mol/kmol | Precontact 25 bar/75 ml | Precontact 30 bar/75 ml |
| $C_6/C_2$ mol/kmol | 32.9 | 32.9 | 49.4 | 49.4 | 56.0 | 49.4 | 49.4 |
| Yield g | 731 | 514 | 740 | 256 | 382 | 0 | 0 |
| Run time min | 58 | 60 | 57 | 70 | 61 | 60 | 60 |
| **Activity kg/g/h** | **3.0** | **1.9** | **3.0** | **1.1** | **0.9** | **0** | **0** |
| Note | | | | Induction time 10 min | | | |

Temperature 80 ºC , Total pressure 20,4 bar, $C_2^-$ partial pressure 7,0 bar, Run time 60 min

The level of deactivation was different depending on the catalyst used. For (nBuCp)$_2$ZrCl$_2$, an approximately one third decrease in the level of activity was observed whereas for (nBuCp)$_2$HfCl$_2$, the effect was enormous, killing the catalyst activity. H$_2$ should not be in pre-contact with metallocene catalysts, especially with (nBuCp)$_2$HfCl$_2$, which can occur in the operation of production scale slurry or solution polymerisation processes.